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Increase in conductivity in 2-(4-peridil)-5-phenyl-1,3,4-oxadiazolium (triphenylphosphine) copper iodide films when exposed to UV radiation

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The paper presents a study of optical, luminescent and electrical characteristics of organometallic compounds based on copper iodide, the method of obtaining, microscopy, and the results of IR spectroscopy of thin-film structures. The results of the current-voltage characteristics of Cu(I) in the ITO–Al contact system are presented. As a result of the analysis of the current-voltage characteristics, it was demonstrated that thin films of copper iodide have rectifying light characteristics under the action of ultraviolet radiation. It is shown that irradiation experimental structures with electromagnetic radiation of the UV range led to an increase in direct currents by 3.5 times.

Keywords: thin films; volt-amp characteristics; quantum efficiency; copper iodide.

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Introduction

During the past decade, multicolor luminescent materials have become a subject of growing interest in the fields of light-emitting diodes, sensors, solar cells, and artificial photosynthesis [1–4]. Organometallic complexes based on copper iodide, i.e. Cu(I) complexes, are attracting increasing attention from researchers as advanced and environmentally friendly materials due to their adjustable structural and photophysical properties [5, 6]. Cu(I) complexes featuring excellent luminescent properties and a high quantum yield at room temperature are promising for materials science and the semiconductor industry [7, 8]. The development of new copper-based Cu(I) systems, especially heteroleptic complexes, is highly motivated, as they represent an attractive alternative to the systems utilizing more expensive platinum-group metals and rare-earth elements [9, 10]. Current

advances in semiconductor manufacturing technologies make a significant and unique contribution to the development of electronic devices [11]. Thin films are mainly fabricated using solution-processing methods, including drop-casting, spin-coating, the doctor-blade technique, and spray-coating [12–15]. Systematic studies on the use of Cu(I) organometallic compounds in the field of semiconductor electronics are clearly insufficient; therefore, the aim of this work was to study the optical, luminescent, as well as resistive properties of Cu(I) complexes based on 2-(4-pyridyl)-5-phenyl-1,3,4-oxadiazole (triphenylphosphine) copper iodide.

Experiment procedure

The objects of the study were the compounds: 2-(4-pyridyl)-5-phenyl-1,3,4-

oxadiazole (triphenylphosphine) copper iodide (see Fig. 1), prepared using a similar procedure [16]. A 20-ml volume of methanol and a 20-ml volume of chloroform were poured into a 100-ml flat-bottomed conical flask. Then, 0.262 g (0.001 mol) of triphenylphosphine and 0.232 g (0.001 mol) of oxadiazole were successively dissolved while being stirred without heating, after which 0.190 g (0.001 mol) of copper(I) iodide was added. Then the reaction mixture was heated to 60 °C and stirred for 15 minutes, after which the heating was turned off and the mixture was stirred for an additional 40 minutes. The reaction mixture was then filtered through a

pleated paper filter. The resulting filtrate was left to evaporate slowly for the target product to settle; due to the high evaporation rate of the solvents, the evaporation vessel was equipped with a thin permeable film to slow down the evaporation process in order to improve the target product quality. Over the next two days, a mixture of the target product and unreacted reagents accumulated on the vessel walls; the target product settled as yellow, rhombic crystals that luminesced yellow-orange under ultraviolet irradiation. The structural formula of the obtained Cu(I) organometallic compound is shown in the inset of Fig. 1.

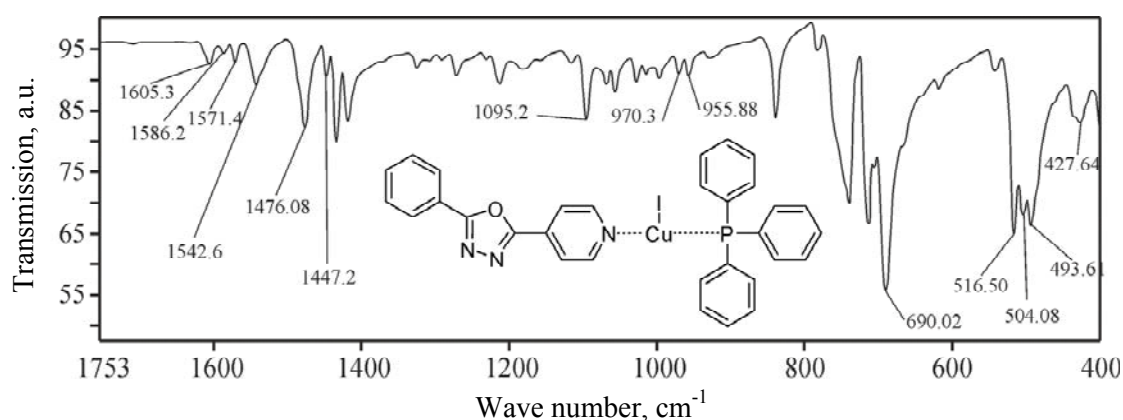


Fig. 1. IR transmission spectra of 2-(4-pyridyl)-5-phenyl-1,3,4-oxadiazole (triphenylphosphine) copper iodide and the molecular structure of the obtained compound (inset).

Thin films were formed from the starting powdered materials using a PE 6900 centrifuge by layer-by-layer deposition. Non-aromatic chloroform CHCl_3 was used as a solvent. The mass of the powdered materials was checked using Sartogism CE124-C high-precision analytical balances. The concentration of the starting materials in the solution was 1 mg/ml. After being thoroughly mixed and held for at least 48 hours at room temperature, 1 ml of the resulting solution was applied using a pipette dispenser onto optically transparent dielectric and conductive substrates. The centrifugation speed was gradually increased to 1500–3000 rpm with an increment of 500 rpm.

IR spectra of the Cu(I) organometallic compound under study were recorded with a PerkinElmer Spectrum Two FTIR spectrometer featuring a Fourier transform range of 8300–350 cm^{-1} and a resolution of 0.5 cm^{-1} . Luminescence spectra were investigated at room temperature with the use of a Fluorolog-FL 3-22

instrument (HORIBA Jobin-Yvon Inc.). To determine the optimal excitation radiation maximum, a standard pulsed excitation technique was used, which involves repeated irradiation of the working layers of organic film structures. Luminescence spectra were measured with account of the excitation maxima parameters. The surface morphology of the thin Cu(I) films was evaluated by reflection and transmission microscopy using a LOMO MII-4M microinterferometer with additional illumination, a semiconductor laser, and an extended optical path onto CCD matrices ranging from $\frac{1}{4}\text{FF}$ to $\frac{1}{2}\text{FF}$ with a resolution of 0.5 to 15 MP. Thermogravimetric analysis (TGA) was performed using a PerkinElmer STA6000 thermogravimetric analyzer.

Conductive properties under direct-current mode were investigated using a Keysight B1500A semiconductor device analyzer. To study the current-voltage characteristics (I-V characteristics) of the Cu(I) organometallic

compounds, the solution was deposited onto thin aluminum films, which were obtained by vacuum deposition on siall and had a thickness of 120 nm and a sheet resistance of 20 Ω /square [15], followed by the formation of an Al-Cu(I)-ITO sandwich structure. Measurements were carried out in the voltage range from of -1 to 1 V. The thin aluminum film forms an ohmic contact with Cu(I), since its work function is comparable to the work function of Cu(I). The geometric parameters of the conductive substrates were 10×10 mm.

Results of experiments and discussion

Primary analysis of the surface of thin copper iodide films showed relative homogeneity of the obtained thin films (Fig. 2a). The thickness of the Cu(I) film was approximately $2 \mu\text{m}$. Individual agglomerations with a diameter of $\sim 40 \mu\text{m}$ were also seen to form on the film surface. The luminescence quantum yield, namely the triplet-level energy values of the corresponding materials, was determined based on photoluminescence spectra. The relative luminescence quantum yield was calculated by the following formula (1):

$$Q = \frac{S}{S_{\text{эТ}}} \times \frac{(1-R)}{(1-R_{\text{эТ}})}, \quad (1)$$

where S is the area under the luminescence spectrum curve, A is the absorbance at the excitation wavelength, and R is the reflectance. Quinine sulfate, rhodamine B, and sodium salicylate were used as references; the measurement accuracy was 10%.

Initially, the excitation spectrum maxima of the Cu(I) organometallic compound were established. The excitation peak for Cu(I) was 465 nm (Fig. 2b). The luminescence spectrum maximum of Cu(I) was observed in the range from 510 to 740 nm (Fig. 2b). The studied organometallic compound exhibited yellow-orange emission with a maximum wavelength of 625 nm. It should also be emphasized that the external quantum efficiency (EQE) of the studied compound was as high as 55.84% (inset of Fig. 2b). As a result, it has been clearly demonstrated that the obtained Cu(I) organometallic compound can potentially be used as an active re-emitting material for semiconductor structures.

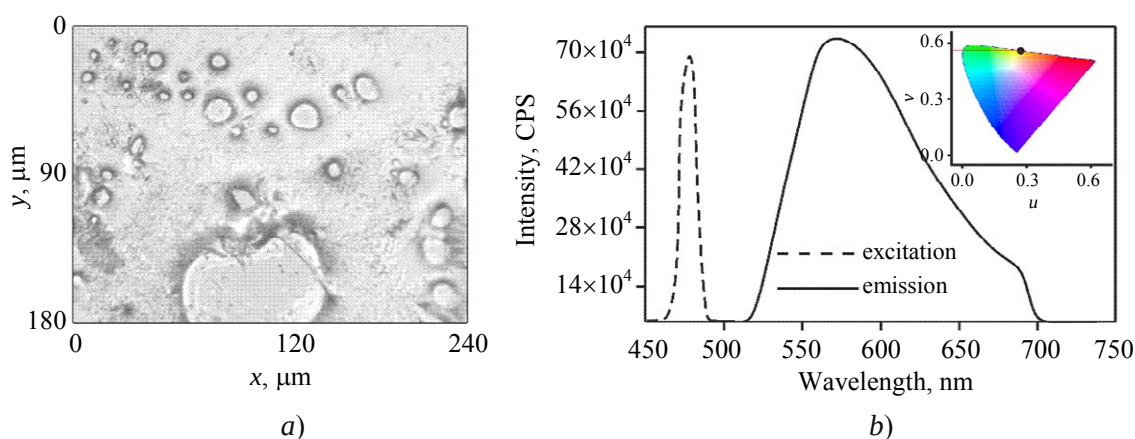


Fig. 2. Surface micrometry of copper iodide (a) and the excitation and luminescence spectra of Cu(I) (b)

Bands lying in the range of 1605.3 – 1447.2 cm^{-1} were recorded in the obtained IR spectrum. Such bands are characteristic of the vibrations of the aromatic ring found in both 2-(4-pyridyl)-5-phenyl-1,3,4-oxadiazole and triphenylphosphine. It is important to note that the band at 1542.6 cm^{-1} exhibits greater intensity compared to the preceding bands, which is specifically typical for aromatic ring vibrations.

Also, a slight shift of the peak characteristic of the Cu(I)–P bond at 1095.2 cm^{-1} can be observed in the spectrum, which arises from the formation of a coordination bond between the copper ion and the donor phosphorus atom of triphenylphosphine. Due to the technical specifications of the instrument, signals with wavenumbers below 400 cm^{-1} cannot be recorded; however, characteristic vibrations for

Cu(I)–I and Cu(I)–N bonds should potentially be found in this region (Fig. 1).

Conductive and photovoltaic properties of the studied structures were measured using a Keysight B1500A semiconductor analyzer with a shielding chamber (Faraday cage). An LED

matrix integrated into the chamber was used as an illumination source. The emission spectrum of the LED matrix is shown in Figure 3a. The total incident power on the sample was approximately 60 mW, and its flux density was about 300 W/m².

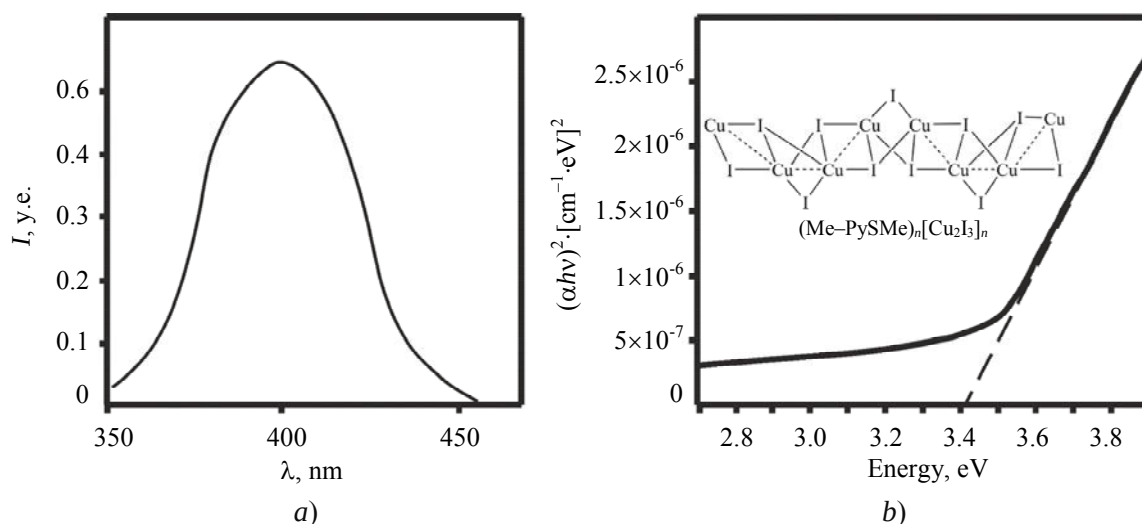


Fig. 3. a) – emission spectrum of the LED matrix, b) – optical band gap of copper iodide

To account for the shift of the fundamental absorption band, an assumption about band-to-band absorption with indirect allowed transitions with an exponent of 2 was made [17, 18].

$$\alpha h\nu = A(h\nu - E_g)^m, \quad (2)$$

where α is absorption coefficient, A is a constant, $h\nu$ is the photon energy, and E_g is the band gap of the material.

The effect of the stoichiometric atomicity of Cu(I) molecules on the shift of the fundamental absorption edge and the change in the band gap of

the organometallic semiconductor was evaluated as 3.4 eV (Fig. 3b). Mass loss of up to 55% accompanied by an endothermic effect was detected in the temperature range of 180–200 °C according to the TGA data (Fig. 4a). This corresponds to the removal of a coordinated water molecule. The compound is thermally stable up to 350 °C. Heating above 350 °C leads to slow decomposition of the sample. Thus, it can be concluded from the obtained results that the compound 2-(4-pyridyl)-5-phenyl-1,3,4-oxadiazole (triphenylphosphine) copper iodide is thermally stable up to 180 °C.

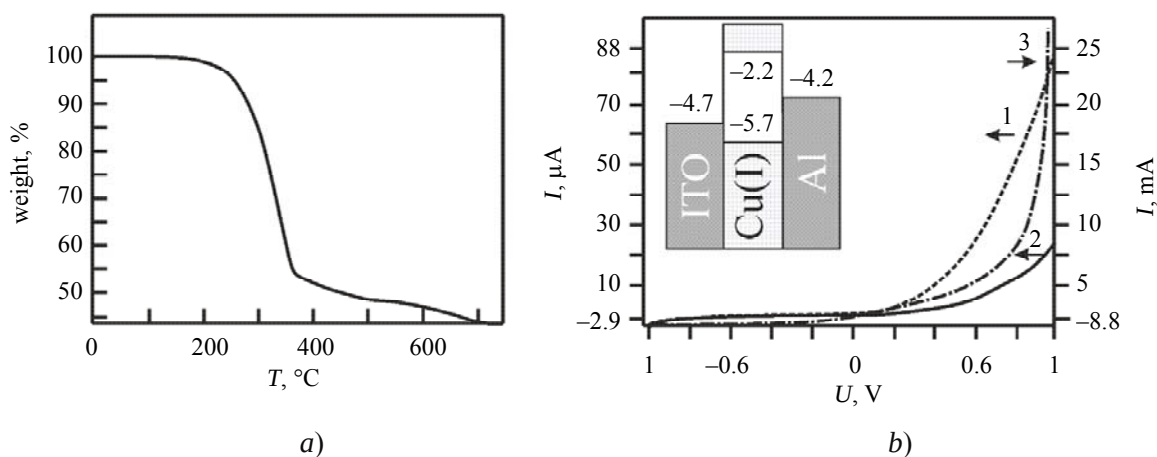


Fig. 4. Thermogravimetric analysis of the obtained Cu(I) compound (a); Dark (2) and light (1) current-voltage characteristics of the ITO–Cu(I)–Al structure (b)

Conductive properties, including photoconductivity, were studied by analyzing current-voltage characteristics (I-V characteristics). Measurements were performed in the voltage range from -1 to 1 V. Figure 4b shows the dark and light I-V characteristics of the ITO-Cu(I)-Al structure (curves 1 and 2), and the ITO-Al contact system (curve 3). The general shape of the current-voltage dependences is nonlinear, asymmetric, and stable within the experimental cycle. Exposure of the Al-Cu(I)-ITO structure to the ultraviolet radiation led to an increase in current in the forward direction from $25\text{ }\mu\text{A}$ to $88\text{ }\mu\text{A}$ due to the generation of photoinduced charge carriers in the copper chain “doped” with iodine (inset of Fig. 3b [19]).

Conclusion

The paper studies the photovoltaic and spectral properties of thin films of the compound 2-(4-pyridyl)-5-phenyl-1,3,4-oxadiazole (triphenylphosphine) copper iodide. The study of IR spectra revealed the presence of numerous

absorption peaks corresponding to this class of compounds. The results of luminescence studies clearly demonstrated the potential of Cu(I) for use as active re-emitting layers, with the quantum efficiency of this material being 55.84%. The excitation maximum of such a complex was observed at a wavelength of 465 nm, with corresponding re-emission in the range of 510–740 nm. The estimated optical band gap was found to be 3.4 eV. The photovoltaic characteristics of the Al-Cu(I)-ITO system, compared with the dark I-V characteristics, showed an increase in forward currents from c $25\text{ }\mu\text{A}$ to $88\text{ }\mu\text{A}$ under UV radiation. The detailed photochemical mechanisms responsible for the large change in electrical conductivity caused by ultraviolet radiation in the polymer appear to be very complex and will be the subject of future research.

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